

# Nano-heteromorphism, structure and relaxation in glassforming Ge-S system

## Part I. Structure and relaxation in condensed germanium disulfide GeS<sub>2</sub>

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On a basis of the developing conception of polymeric polymorphous structure of glass and glassforming liquid were analyzed the structure and relaxation processes in crystalline, liquid and glassforming states of germanium disulfide GeS<sub>2</sub>.

(Received October 16, 2006; accepted November 2, 2006)

**Keywords:** Ge-S chalcogenide system, Nano-heteromorphism, GeS<sub>2</sub>

### 1. Introduction

The Ge-S system can exist in three varieties of condensed state – crystal, liquid and glass ones.

One of the goals of this work is to show the genetical intercommunication of all these states and their structures as well.

In part I of this work we will consider only the individual chemical compound GeS<sub>2</sub> and the relaxation processes proceed in one in all three mention states.

### 2. A new paradigm of glass structure

For a consideration of the structure any glass-forming substance we use as basis the conception of polymeric nano-heteromorphous glass structure (CPNHGS) [1].

Nano-heteromorphism is a concurrent existence in non-crystalline substance of structurally different fragments of nanometric dimensions of crystal lattices without a long-range order [2].

The foundation of CPNHGS is its particular case – concept of polymeric-polymorphous structure of glass and glass-forming liquid (CPPSGL) of individual chemical substance, ICS (element or chemical compound) [3].

The CPPSGL includes the following ideas from earlier conceptions [4]:

- polymeric structure (Mendeleev [5], Sosman [6], Tarasov [7]);
- absence of a long-range order (LRO) in continuous random glass-forming network (Zachariasen [8]);
- chemical ordering of the glass-forming network (Lucovsky and Hayes [9], Wright et al. [10]);
- influence of crystalline polymorphous modifications (PMs) on glass structure and properties (Frankenheim [11], Lebedev [12], Goodman [13]).

The CPPSGL rejects the following ideas of earlier conceptions:

- the continuous random network consisting of randomly located separate atomic polyhedrons [8], for example SiO<sub>4/2</sub> in v-SiO<sub>2</sub>;

- presence in glass of a single short-range order (SRO);

- presence in glass of a single intermediate-range order – IRO (having no strict definition until our works [14-16]);

- presence in glass of micro-crystals (crystallites).

The CPPSGL introduces the following new ideas:

- the process of one-component vitreous substance (that is ICS) formation is the process of generation, mutual transformation and copolymerization of structural fragments (polymorphoids) of various PMs of crystal substance without an LRO in disordered polymeric-polymorphous structure (network, tangle of chains, ribbons, etc.) of glass;

- the polymorphoid as a bearer of a strictly defined IRO of concrete crystalline PM; IRO is a stereometrically determined arrangement (topology) of SROs in the boundaries of polymorphoid, characterized by parameters of all SROs and dihedral angles, the IRO, at least along one of the crystallographic axes has dimensions less than two periods of crystal lattice, otherwise the polymorphoid becomes a crystallite – a minimum fragment of crystalline substance;

- presence in glass and glass-forming liquid of not less than two SROs and not less than two IROs pertaining to different crystalline PMs;

- copolymerization of polymorphoids of different PMs resulting in formation of a continuous network that is disordered (random) on the macro- and micro-level and ordered on the nano-level (levels of short-range and intermediate-range orders);

- inter-transformation of polymorphoids of different PMs and alteration of their concentration ratio in glass-forming liquid and glass under influence of external

impacts and time causing alteration of their structure and properties even up to their crystallization as this or that PM;

- a glass-forming individual chemical substance is the continuum – the interrupted connected multitude – of atomic structures characterized by the concentration ratio of copolymerized polymorphoids of different PMs.

The CPPSGL represents the synthesis of objective features of existing hypotheses and models of glass structure and new ideas into a single noncontradictory conception of glass structure. A new paradigm of glass structure has been created [4, 17, 18].

### 3. Crystalline polymorphous modifications and phase transitions in germanium disulfide $\text{GeS}_2$

In compliance accordance with the phase diagram of Ge-S system (Fig. 1 [19-21]) germanium disulphide  $\text{GeS}_2$  exists at normal pressure in two polymorphous

modifications – high-temperature (HTPM,  $\alpha$ -modification) and low-temperature (LTPM,  $\beta$ -modification) [22, 23]. The HTPM has two-dimensional layered structure in which  $\text{GeS}_{4/2}$  tetrahedrons, connected in vertexes (corner-shared tetrahedrons - CST), form chains connected by bridges from pairs of tetrahedrons, connected in edges (edge-shared tetrahedrons - EST). In HTPM there are equal numbers of CSTs and ESTs. The HTPM has the melt temperature of 840 °C [24] (850 °C [20]).

The LTPM is constructed of tetrahedron chains arranged along directions [001] and [101] and connected by only CST in the three-dimensional network [25].

Schematic image of atoms network connection is shown in Fig. 2, 3 [25].

In addition there are other PMs obtained at high pressure.

The main feature of  $\text{GeS}_2$ -PMs are collected in Table 1 [26].

Table 1. Conditions of production and crystal structure in Ge-S system [26].

Substance	Conditions of production	Type of crystal structure and space group	Parameters of elementary cell	Literature
$\alpha$ - $\text{GeS}_2$ (high-temperature modification)	Synthesis from elements	Rhombic $\text{Pmmn-D}_{2h}^{13}$	$a=6,87$ $b=11,67$ $c=22,38 \text{ \AA}$ $Z=24$	[24]
		Monoclinic $\text{P2}_1/\text{c}$	$a=6,720$ $b=16,101$ $c=11,436 \text{ \AA}$ $\beta=90,88^\circ$ $Z=16$	[22]
$\beta$ - $\text{GeS}_2$ (low-temperature modification)	Synthesis from elements	Monoclinic $\text{Pc}$	$a=6,875$ $b=22,55$ $c=6,809 \text{ \AA}$ $\beta=120,45^\circ$	[23]
$\gamma$ - $\text{GeS}_2$	High pressure (3-6,5 GPa) Temperature 900-1000 °C; High pressure (1-5 GPa) Temperature 400-500 °C, 70-90 hours	Tetragonal	$a=5,480$ $c=9,14 \text{ \AA}$ $Z=4$	[27, 28]
$\delta$ - $\text{GeS}_2$	High pressure (6-7 GPa) Temperature 500 °C, 40 h;	Structural type $\text{CdJ}_2$	$a=3,456$ $c=10,89 \text{ \AA}$	[28]
GeS	Synthesis from elements	Rhombic $\text{Pcmn-D}_{2h}^{16}$	$a=4,38$ $b=3,82$ $c=10,89 \text{ \AA}$	[29]

$\text{GeS}_2$  is liable to enantiotropy polymorphous transformation  $\text{HTPM} \leftrightarrow \text{LTPM}$  which is characterized by certain temperature of polymorphous transformation ( $T_{tr}$ ).

$T_{tr}$  is equal to 520 °C on the side of GeS and to  $497 \pm 3$  °C on the side of S (Fig. 1 [19-21]).

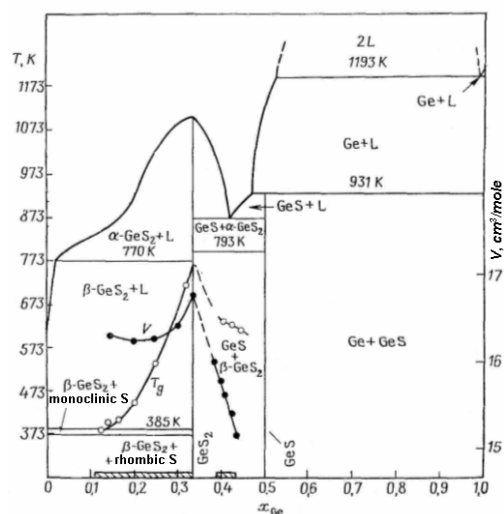


Fig. 1. The phase diagram of Ge-S system [9-21].  $V$  – molecular volume;  $T_g$  – glass transition temperature.

#### 4. Structure of vitreous $\text{GeS}_2$

Several structural models of vitreous  $\text{GeS}_2$  are known.

In 1979 Bridenbaugh, Phillips, Griffiths and others [30] proposed a layered structure for v- $\text{GeS}_2$  constructed from large ribbon-like structural units (clusters) called by the authors “outrigger-raft”. These structural units are obtained by extraction from the layer of HTPM. Along edges of ribbons the S atoms are joined in pairs by S-S bonds.

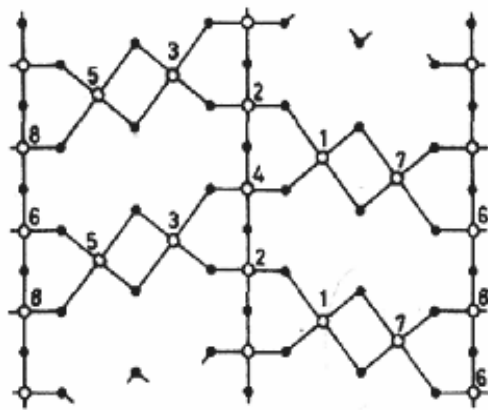


Fig. 2. Schematic illustration of network connection in a layer of the high temperature form. Open circles show Ge atoms, and closed circles, chalcogen atoms. Numbers from 1 to 8 indicate the different  $\text{GeX}_4$  tetrahedra sites in a unit cell in the layer. Linear chains  $(-2-4-2-4-)$  and  $(-6-8-6-8-)$  along  $[100]$  direction are connected by bridges  $(1-7)$  and  $(3-5)$  [25].

In the beginning of eighties works of Lucovsky and others [31] were published where authors proposed models of v- $\text{GeSe}_2$  and v- $\text{GeS}_2$  structures containing both tetrahedra, connected along edges, and tetrahedra,

connected in vertices that is the model of chemically ordered continuous random network.

In 1986-87 Sugai [32, 33] proposed a new stochastic random network model of germanium and silicon chalcogenides. The stochastic random network model is characterized by one parameter  $P$  representing the probability of the ratio of chemical bonds of edge-shared tetrahedrons of  $\text{GeX}_4$  and chemical bonds of corner-shared tetrahedrons. The stochastic model gives, in the author's opinion, equal possibilities for photo-induced crystallization in two different crystalline phases while the “outrigger-raft” model – only one possibility.

Sugai has constructed his model from stochastically joined in three-dimensional network two types of “molecules”: tetrahedrons  $\text{GeS}_{4/2}$  and edge-shared tetrahedrons  $\text{S}_{2/2}\text{GeS}_2\text{GeS}_{2/2}$  [32, 33] leaving aside the problem of short-range and intermediate-range ordering.

According to the CPPCSGL concept, the feature of the short-range ordering in vitreous  $\text{GeS}_2$  is presence, mainly, of two types of SRO, with two different atoms taken as a reference point. In the first case it is a germanium atom surrounded in tetrahedra by four sulphur atoms  $\text{GeS}_{4/2}$ , and, in the second case, it is a sulphur atom surrounded by two germanium atoms  $\text{SGe}_{2/4}$ . As we can see, both SROs are in agreement with the principle of the chemically ordered network [9, 10, 31, 34]. It must be noted straight away that each of these SROs has its own variations: differences in average bond lengths Ge-S and interbond angles S-Ge-S and Ge-S-Ge in the tetrahedra joined by only corners in LTPM (Ge-S (Å)-2.24; S-Ge-S ( $^\circ$ )-109.4; Ge-S-Ge( $^\circ$ )-101.5) and the tetrahedra joined corners and edges in HTPM (Ge-S (Å)-2.21; S-Ge-S ( $^\circ$ )-109.5; Ge-S-Ge( $^\circ$ )-95.7) [35].

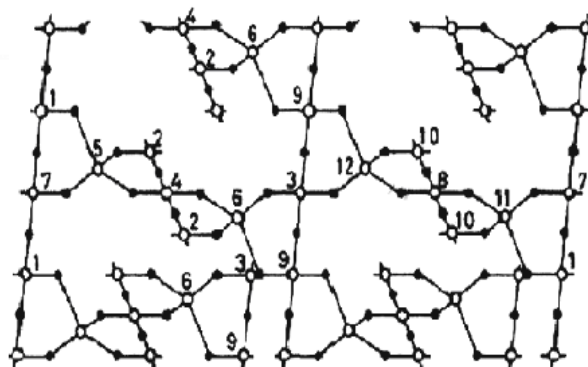


Fig. 3. Schematic illustration of network connection in low temperature form. Open circles show Ge atoms, and closed circles, chalcogen atoms. Numbers from 1 to 12 indicate the different  $\text{GeX}_4$  tetrahedra sites in a unit cell. There are two kinds of linear chains  $(-1-7-1-7-)$ ,  $(-3-9-3-9-)$  along  $[001]$  direction, and  $(-2-4-2-4-)$  and  $(-6-8-6-8-)$  along  $[010]$  direction. These chains are not included in the same plane, and they are connected mutually by corner-sharing tetrahedra 5, 6, 11, and 12 in a 3-dimensional way [25].

The intermediate-range ordering in v- $\text{GeS}_2$  is characterized mainly by two alternating intermediate-range orders: IRO inherent to HTPM (two-dimensional layered structure) and IRO adopted from LTPM (three-

dimensional network structure). Each of these IROs includes variations of the short-range order corresponding to one or another PM.

On the base of mentioned works [25,31-35], from positions of the conception of polymeric polymorphous-polymorphoid structure, the conclusion has been made that the structure of vitreous  $\text{GeS}_2$  (and glass-forming liquid) is formed by co-polymerized (de-polymerized) polymorphoids (structural fragments without a long-range order) of layered (two-dimensional) HTPM and three-dimensional LTPM which are joined in glass in a single three-dimensional network characterized by alternation of mainly two intermediate orders inherent to HTPM and LTPM.

The comparison of Raman spectra of crystal HT-, LTPMs and v- $\text{GeS}_2$  (Fig. 4 [25,36]) serves as good illustration of this inference.

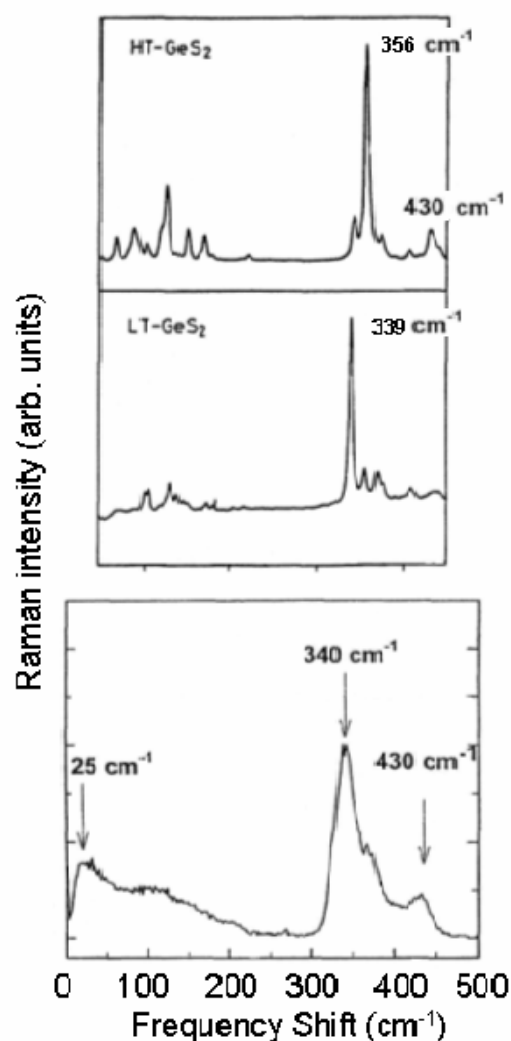


Fig. 4. Raman spectra of HT-, LT-  $\text{GeS}_2$  [25] and v- $\text{GeS}_2$  [36].

The most intense peak  $356\text{ cm}^{-1}$  of HT- $\text{GeS}_2$  and peak  $339\text{ cm}^{-1}$  of LT- $\text{GeS}_2$  [25] noticeable appear themselves

within the boundaries of v- $\text{GeS}_2$  broad bond ( $\sim 320 - \sim 380\text{ cm}^{-1}$ ) [36].

The  $430\text{ cm}^{-1}$  mode is observed in both the HTPM and v- $\text{GeS}_2$  spectra. This mode was associated with the edge-sharing tetrahedra on the basis of a vibrational analysis [37].

There are contradictions concerning the structure interpretation of v- $\text{GeS}_2$  such as whether the network is chemically ordered [9,10,31,34,38] or whether this order is broken [30,39,40]. So the  $430\text{ cm}^{-1}$  mode has been considered in [39] as the signature of chemically disordered S-S bonds.

Vibration density-of-states calculations [41] identify this mode with the S-S stretch of dimers at the edges of outrigger raft clusters which were proposed in the molecular cluster models [30].

The structure of v- $\text{GeS}_2$  was examined by Raman scattering,  $^{119}\text{Sn}$  Mössbauer spectroscopy and temperature-modulated differential scanning calorimetry. The results show that the stoichiometric glass v- $\text{GeS}_2$  is chemically disordered. Raman scattering places mode strengths of corner-sharing  $\text{Ge}(\text{S}_{1/2})_4$  tetrahedra, ethan-like  $\text{Ge}_2(\text{S}_{1/2})_6$  units and the distorted rock salt  $\text{Ge}(\text{S}_{1/6})_6$  units at approximately 93,4:3,6:3,0 [40].

It follows that glass network of v- $\text{GeS}_2$  is chemically disordered and homopolar bonds Ge-Ge and S-S are exist in this glass.

On the other hand no compelling evidence could be found for a substantial deviation from heteropolar Ge-S bonding when the total structure factor for v- $\text{GeS}_2$  has been measured by using the neutron diffraction [42].

In any case, either the networks is chemically ordered or this order is broken, the principal feature of glass structure is the combination in one the copolymerized structural fragments of different polymorphous modifications without long-range order (polymorphoids).

## 5. The relaxation processes in glass-forming liquid and glassy $\text{GeS}_2$

### 5.1. The relaxation of the glass-forming liquid

CPPSGL by the examples of Se [43],  $\text{SiO}_2$  [18], v- $\text{GeS}_2$  [2],  $\text{BeCl}_2$  [44, 45],  $\text{H}_2\text{O}$  [3] compelling witnesses that associative liquid consist of different PM polymorphoids. Ones are conventionally HT- and LT-polymorphoids. The fact of generation of both HT- and LP- polymorphoids in the melt is very important: cooling such melt will lead to copolymerization of structural fragments of different PMs lattices without LRO that obstructs melt crystallization and promotes glass formation.

A liquid state at certain temperature is characterized by a certain concentration ratio of polymorphoids (CRP) of different PMs. At temperature changes the inverse reaction of polymorphoids inter-transformation takes place: HTPM  $\leftrightarrow$  LTPM, and CRP changes (Fig. 5).

During cooling of liquid below the melting temperature there are two main processes that take place. The first one is the process of co-polymerization of

polymorphoids of different PMs leading to viscosity increase and obstructing melt crystallization.

The second process is conditioned by the fact of passing of liquid of the HTPM stability range and LTPM instability range in the interval  $T_m$ - $T_{tr}$  (Fig. 5). It is naturally to expect that in these conditions polymorphoids inter-transformation will be shifted in direction of HTPM fragments concentration increase, and LTPM fragments disintegration is becoming apparent as the process of depolymerization of super-cooled liquid going along with the main process of its polymerization.

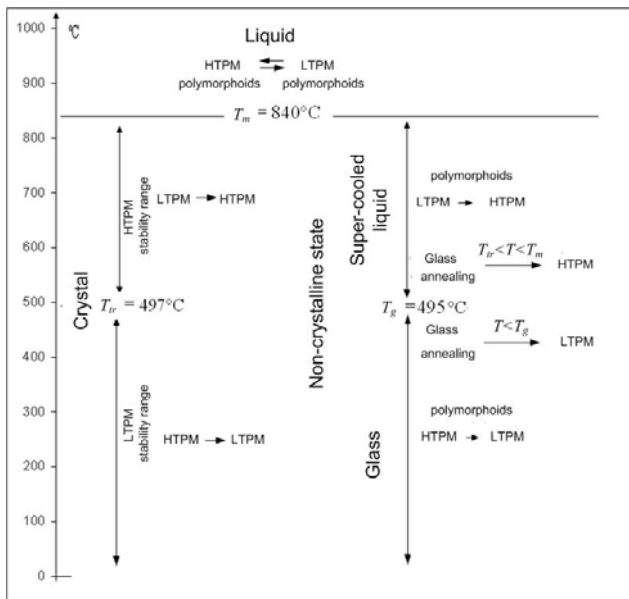


Fig. 5. Schematic illustration of relaxation processes in condensed  $\text{GeS}_2$  [this work].

If the cooling rates is less than critical ( $V_{cr}$ ) one which equals for  $\text{GeS}_2$   $17.5 \text{ K}\cdot\text{s}^{-1}$  at water quenching of 10 g melt [46, 21], all LTPM polymorphoids have enough time to transform in HTPM polymorphoids before reaching the temperature range where LTPM is stable and HTPM is unstable that is at  $T < T_{tr}$ . In this case super-cooled liquid crystallizes as HTPM.

At high cooling rate the first process (co-polymerization) prevails, supercooled liquid passes the LTPM instability range, having conserved, along with increasing HTPM polymorphoids concentration, LTPM polymorphoids concentration which is sufficient for glass formation. The glass transition temperature at the cooling of melt ( $T_g$ ) is the temperature of stopping of disintegration of non-stable LTPM polymorphoids, the temperature of the termination of copolymerization process of polymorphoids of HTPM and LTPM, the temperature of glass formation. Then the substance is cooled being in glass state.

Long aging of cooled substance at temperature below  $T_g$  in the LTPM stability range can lead to glass crystallization as LTPM.

Thus, relaxation of  $\text{GeS}_2$  glass-forming liquid at cooling, depending on change of the temperature factor, can results in formation of HTPM or LTPM or glass [2, 4].

## 5.2 Relaxation processes in v- $\text{GeS}_2$ at the heating

Fig. 6 [47] shows Raman spectra of bulk-like samples of  $\text{GeS}_2$ , prepared at different temperatures. There is a significant change in the spectra between  $80^\circ\text{C}$  and  $100^\circ\text{C}$ . At lower temperatures the broad features of non-crystalline  $\text{GeS}_2$  are observed. The features are analogous to ones in non-crystalline sample spectra (see Fig. 4). At higher temperature ( $>80^\circ\text{C}$ ) suddenly much sharper features occur, i.e. an abrupt structural phase transition occurs. The spectra are analogous to ones of low-temperature PM  $\alpha\text{-GeS}_2$  [25].

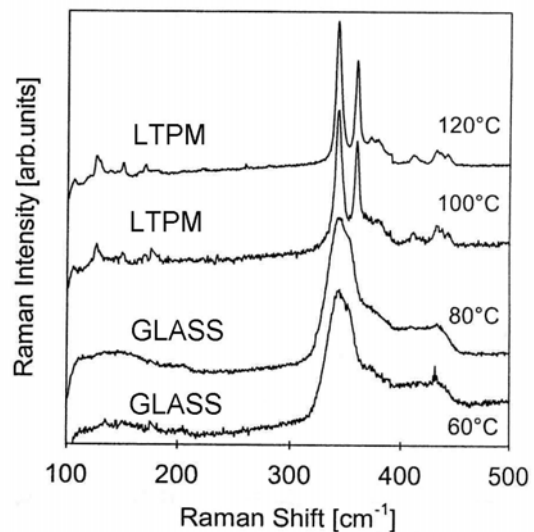


Fig. 6. Raman spectra of  $\text{GeS}_2$  at different temperature [47].

From the point of view of CPPSGL the crystallization process in these conditions is lawful, because the LTPM polymorphoids placed in glass (together with HTPM polymorphoids) at the temperature below  $T_{tr}$  (Fig. 5) are unstable and transform to HTPM polymorphoids.

It is known that for individual substances the transition from HTPM to LTPM is followed by exothermal effect and the transition from LTPM to HTPM is followed by the endothermal effect [48].

This means that the crystallization of v- $\text{GeS}_2$  below  $T_g$  proceeds with exoeffect. The example of such kind behavior is v- $\text{GeSe}_2$ . In the temperature range of  $250\text{--}350^\circ\text{C}$  which precedes the glass transition temperature smooth exothermal rise is observed on the thermogram of DSC [49]. This effect was interpreted [2] as the transformation process of a part of containing in glass HTPM polymorphoids in LTPM polymorphoids – the process that can be identified as the latent period preceding LTPM-  $\text{GeSe}_2$  crystallization.

The analogous effects are observed below  $T_g$  in glassforming  $\text{H}_2\text{O}$  [50, 3] and selenium [51, 43].

And finally, direct corroboration of exoeffect at heating of  $\text{GeS}_2$  below  $T_g$  has been obtained in our opinion in [40] (Fig. 7). The exothermic lowering on DSC-curve of

GeS<sub>2</sub> below  $T_g$  (onset) in the range from ~473 to ~493 °C has been recorded.

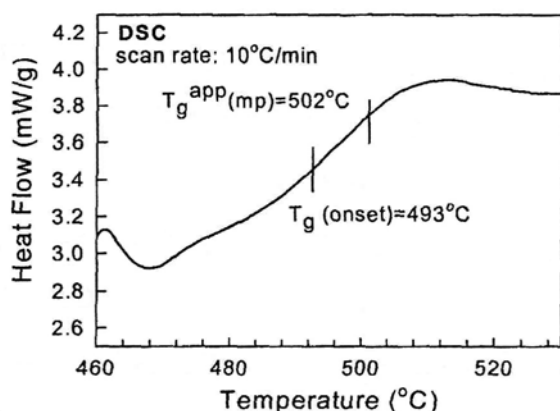


Fig. 7. Differential scanning calorimetry scan GeS<sub>2</sub> glass [40].

These data correlate well with the data on crystallization v-GeS<sub>2</sub> below  $T_g$  [47] proceeding with the exoeffect apparently.

At the temperature  $\geq T_g$  ( $\approx T_{tr}$ ) in v-GeS<sub>2</sub> is observed the active endothermic effect (Fig. 7). In the context of CPPSGL one is interpreted as the transformation of polymorphoids LTPM into ones HTPM. It is naturally since higher  $T_g$  heated glsss come into the range, were LTPM is unstable and HTPM is stable (Fig. 5).

Thus, the glass formation temperature at heating ( $T_g^+$ ) is nothing else but the temperature of the beginning of the active stage of the transformation of low-temperature PM polymorphoids into high-temperature PM polymorphoids, accompanied by the decomposition of the formers, i.e. by the rupture of chemical bonds in glass, its depolymerization, its viscosity decrease and the high-temperature PM polymorphoids format.

The data, reported above, testify that  $T_g$  is genetically related with temperature of polymorphous transformation  $T_{tr}$  in crystal substance, that  $T_g$  in glass is analogue to  $T_{tr}$  in crystal substance.

## 6. Conclusion

The analysis of the structure and relaxation processes in crystal, liquid and glassforming germanium disulfide GeS<sub>2</sub> show the complete agreement with ideas developed by the conception of polymeric-polymorphoid structure of glass and glassforming liquid.

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